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Title: **A Process for Preparing Self-Adherent Hydrogels**

An Examination Request according to § 44 Pat. Law has been filed.

Abstract

The invention deals with a radicalic polymerization of a photo-polymerizable, solvent-free starting mixture by means of a UV-radiation in the wavelength range from 180 to 400 nm for preparing self-adherent hydrogels, whereby the energy needed for initiating the polymerization, is provided by a monochromatic radiation of a laser. The polymerizable, solvent-free starting mixture is comprised of the following components:

- A- a vinyl carboxylic acid,
- B- an alkyl (meth)acrylate with 1 to 12 carbon atoms in the alkyl group,
- C- a polyoxyalkylene with a molecular weight of up to 2000 Dalton, and glycerin or its esters,
- D- a hydroxyl groups containing amine,
- E- a photo-initiator.

DESCRIPTION

The invention deals with a process for preparing self-adherent hydrogels (PSA-hydrogels) by means of a polymerization of a solvent-free monomer mixture, as well as also with their application as medical wound covers.

A number of hydrogel wound covers have been on the market, which exhibit a high absorption capability for wound secretions, whereby a healing of the wound will be assured within a few days under the exclusion of bacteria.

However, these hydrogels exhibit various disadvantages, which will substantially limit their practical application. For instance, these hydrogel materials will not exhibit a sufficient mechanical stability after the absorption of any excretion of a wound. These gels will often be dissolved at the body temperature, and a complete residue-free removal from the wound will often not be possible. In addition, these gels exhibit often an insufficient transparency, whereby a continuous observation of the healing process will be difficult without an exchange of the wound cover.

For eliminating these shortcomings, it has already been attempted to prepare these hydrogels by a polymerization reaction. The energy needed in this case, was introduced into the starting monomer mixture by means of a spectral UV-radiation (UV-lamp).

For instance, in DE 35 06 534, a UV-initiated polymerization of (meth)acrylamide and vinyl sulfone derivatives has been described, which however, did not yield flexible materials suitable for preparing hydrogels.

Furthermore, in US 4 620 954, polymers of N-vinylpyrrolidone and phenylethyl methacrylate prepared by a UV-initiated polymerization, has been described. These polymers are indeed transparent, but do not exhibit any adhesive properties.

In DE-A 38 25 366, a continuous process has been described for preparing an acrylate polymer gel, whereby a layer of the monomer solution is subjected to a radiation by light. This photo-polymerization process has a series of disadvantages, such as e.g. a needed reduction of the dissolved oxygen content in the monomer solution to less than 1 mg/liter or a maintaining of an oxygen concentration in the gas-phase of an air-tight chamber above a moving carrier substrate to a value of not more than 1 vol.-%.

In US 4 189 370, a polymer gel has been described, which is produced by a radicalic polymerization of N-methylolacrylamide with bifunctional allyl- or acrylate derivatives. The polymerization will be initiated by means of peroxides or a UV-radiation.

In EP-A 072 213, a water-containing copolymer gel has been described, which is based on acrylamide/(meth)acrylic salts admixed with kaolin, talc, etc. to be used as a "flow agent".

In JP 60 149 419 and JP 60 149 411, a gel has been described consisting of polyfunctional UV-curable polyacrylates and polyesters.

In US-A 4 790 919, photo-polymerizable gels based on acrylates, have been described.

In JP 63 081 112, a UV-curable gel has been described, which is comprised of an urethane acrylate and N-vinylpyrrolidone.

In US-A 4 914 173, a UV-crosslinkable acrylated polyurethane gel has been described.

In EP-A 327 304 deals with electrically conductive gels based on UV-curable urethane-acrylate oligomers. For obtaining the electric conductivity, $MgBr_2$ was added as an electrolyte.

In US-A 5 141 973, a method for preparing a poly-(vinyl alcohol) gel has been described. For forming the gel, the PVA-molecules have to be physically excited. As the excitement source, a laser radiation is employed.

In JP 2 173 102, a gel has been mentioned, which is composed of a partially hydrolyzed acrylamide polymer. The crosslinking of the gel is carried out by means of a UV-radiation.

In EP-A 396 246, a UV-curable system has been described, in which an acryloyloxy-functional, a mono-acryloyloxy-functional and a non-functional poly-(diorgano siloxane) are used.

In JP 3 192 106, a UV-curable gel has been described, which is composed of hydroxyl groups containing (meth)acrylates (urethane (meth)acrylates), unsaturated derivatives with an ethylene structure, resins and photo-initiators.

In JP 3 192 107, a UV-curable gel has been described based on N-substituted acrylamides.

In CA-A 2 037 703, a process has been described for preparing contact lenses, whereby a laser is used for initiating the crosslinking or polymerizing reaction. The contact lenses are comprised of hydroxyethyl methacrylate. The polymerization is carried out in an oxygen-free or an inert atmosphere.

The objectives to be achieved by the present invention deal with the development of self-adherent, wound secretion absorbing hydrogels, which do not show the aforementioned disadvantages, as well as with a process for their preparation, whereby the hydrogels are to exhibit a high absorption capacity for any exudation of wounds and are to maintain a sufficient mechanical strength after the absorption of the exudation, and are to have a sufficient transparency for permitting an unrestricted observation of the wound.

These objectives have been achieved according to the invention by a process for preparing self-adherent hydrogels by a radicalic polymerization of a photo-polymerizable, solvent-free starting mixture by means of a UV-radiation in the range from 180 to 400 nm, whereby the energy needed for initiating the polymerization reaction, is introduced by means of a monochromatic radiation of a laser, wherein the polymerizable, solvent-free starting mixture contains the following components:

- A- a vinyl carboxylic acid, 30 to 60 weight-%,
- B- an alkyl (meth)acrylate with 1 to 12 carbon atoms in the alkyl group, 10 to 30 weight-%,
- C- a polyoxyalkylene with a molecular weight of up to 2000 Dalton, and glycerin or its esters, 10 to 40 weight-%,
- D- a hydroxyl groups containing amine, 10 to 20 weight-%,
- E- a photo-initiator, 1 to 5 weight-%.

The hydrogels prepared according to the invention exhibit a good adhesion at the locale of application, an excellent absorption capability for liquids, good mechanical properties and a satisfactory transparency.

The starting mixtures suited for the photo-polymerization according to the invention, contain a vinyl carboxylic acid, which will assure a sufficient absorption of a wound exudation due to the hydrophilicity of the present carboxylic groups.

Besides the acrylic- and methacrylic acid, other acids suited for preparing hydrogels with the desired properties, are e.g. β -acryloyloxy propionic acid, vinyl acetic acid, aconitic acid, trichloroacrylic acid, dimethylacrylic acid, crotonic acid, fumaric acid, cinnamic acid and itaconic acid. Among these compounds, the acrylic-, methacrylic- and β -acryloyloxy propionic acid, have been found particularly useful.

Furthermore, the polymerizable starting mixtures contain also olefinic-unsaturated monomers, preferably derived from the family of acrylates, i.e. derivatives of the acrylic acid containing substituents in the 1- and/or 2-position. For preparing self-adherent hydrogels, all these derivatives are suited, which will yield homo- or copolymers having a relatively low glass-transition temperature. The esters of the acrylic and methacrylic acid are the preferred compounds, from which the following esters shall be mentioned as examples: Methyl-, ethyl-, propyl-, isopropyl-, butyl-, isobutyl-, hexyl-, heptyl-, n-octyl-, iso-octyl-, 2-ethylhexyl-, 2-methylheptyl-, nonyl-, isononyl acrylate, decyl-, isodecyl- or dodecyl (meth)acrylate.

For providing the hydrogels with soft and elastic properties and for improving the hydrophilicity, the starting mixture contains also polyoxyalkylenes with a molecular weight of up to 2000 Dalton, glycerin or its esters.

Among the polyoxyalkylenes, the polyoxyethylenes, polyoxypropylenes and copolymer of ethylene oxide and propylene oxide are employed with a molecular weight of up to 2000 Dalton. Preferably, poly-(ethylene glycol) 200, poly-(ethylene glycol) 300, poly-(ethylene glycol) 400, poly-(ethylene glycol) 600, poly-(propylene glycol) 400 and poly-(propylene glycol) 1020, are employed.

Glycerin and its esters have been found particularly useful due to the good physiological compatibility.

These polyoxyalkylenes and also the glycerin and its esters are practically not volatile, which means an advantage and is of a great significance in regard to the application as a plasticizer and humectant.

For improving the mechanical properties and the water absorption capability of the hydrogel by a neutralization of the carboxyl groups of the vinyl carboxylic acid by a reaction between the carboxyl- and amino groups, the polymerizable, solvent-free starting mixture is admixed with hydroxyl groups containing amines, selected from the group of diethanolamine, triethanolamine, N-methyl diethanolamine, tri-isoethanolamine, 2-amino-2-methyl-1,3-propanediol, tris-(hydroxymethyl) aminomethane or dimethyl ethanolamine.

Since the C=C double-bond contained in the mixture, cannot be directly activated by the UV-light, the presence of at least one photo-initiator is essential. These compounds are capable to

absorb the UV-radiation energy under the formation of radicals to initiate, thereby, the polymerization reaction. For carrying out the invention, it is necessary, that the photo-initiators will show an absorption at the emission wavelength of the employed laser equipment, i.e. the photo-initiators are to be selected depending on the type of laser. For the wavelength range from 180 to 400 nm, numerous photo-initiators are available including e.g. the following compounds: Acetophenone, benzophenone, hydroxyalkyl phenone, α -halogenketones, thioxanthenes, fluorenone derivatives and Michler's ketone.

By using the monochromatic radiation of a laser for initiating the polymerization, it is possible to introduce energy into the starting mixture to be polymerized and composed according to the invention to such an extent, as not obtainable by the use of conventional UV-lamps. Since at the one hand, the rate of polymerization will depend among others on the extent of this initial energy, the laser-initiated polymerization will provide a process for preparing pressure-sensitive adhesive materials (self-adherent adhesive materials), by which the shortcomings of the state of the art, will be eliminated. In the publication "Lasers and Photopolymers" by C. Carre et al., Laser Chem. 10, 349-366 (1990), an overview on the laser-induced polymerization is presented. As described, derivatives of the acrylic acid have already been studied, whereby in particular multifunctional monomers were used for curing surface coatings. A mass-polymerization for preparing self-adherent adhesive materials, has not been mentioned.

The laser to be used according to the invention will emit a radiation in the wavelength from 180 to 400 nm. The energy output may be delivered in a continuous form or in an intermittent (pulsating) form. As a continuous laser, the ion-krypton /argon laser (about 350 nm) shall be mentioned or also the ion-helium /cadmium laser (325 nm). The pulsating lasers offer the advantage of a higher impulse energy in the UV-range. This group of lasers include e.g. the so-called excimer-lasers, which are primarily operated with fluorine or a noble gas /halogen blend. As typical representative lasers, the ArF- (193 nm)-, the KrF (248 nm)-, XeCl- (308)- and the XeF- (351 nm)-laser shall be mentioned.

Furthermore, the pulsating Nd:YAG- laser may also be employed in this case, since its emission may be shifted into the UV-range (266 and 365 nm) by a doubling of the frequency. A comprehensive table 5 listing all the available gas-lasers emitting in the range 180 - 400 nm, is presented in the "Handbook of Laser Science and Technology", vol. 2, pp. 497 - 500, CRC-Press, Boca Raton, 1985, to which an explicit reference shall be made. The aforementioned numbers in parentheses refer to the particular emission wavelength.

The duration of the impulse at these typical lasers is in the range of $50 \cdot 10^{-9}$ seconds (50 nanoseconds), whereby the impulse sequence frequencies are adjustable up to several hundreds Hz. The total number of emitted impulses is also programmable. The mean energy output of these lasers may be in the order of up to 100 W. However, in a pulsating operation, energy outputs of about 20 Megawatt may be achieved, whereby energy densities of more than 1 Gigawatt per square-centimeter (10^9 Watt /cm²) will be obtained. The obtainable impulse energy with several hundreds mJoule would be several times higher than the radiation energy of a UV-lamp at the respective wavelength. The energy values listed in this context for UV-lamps, will always refer to the entire spectral range and not to a particular wavelength.

For carrying out the process according to the invention, which is preferably performed in a continuous manner, the flowable liquid composition may be coated onto a carrier substrate in the

desired layer thickness as a full-area coating or also in the form of a pattern by using e.g. a coating knife, coating rolls or cylinders or by means of a wide-slot orifice. The layer thicknesses may be in the range from 50 to 5000 μm , preferably from 100 to 3000 μm . As the carrier substrate, all flat areal substrates are suited having a surface, which will permit a removal of the prepared self-adherent hydrogel. At the selection of the material for the preferably film-like substrate, polymeric materials may be selected, such as polyethylene, polypropylene, polyesters and polyamides, or also paper, if their surfaces are adhesion-release treated e.g. by means of a silicone coating. Moreover, the substrates may also consist of metal foils or textile substrates. Films of poly-(tetrafluoroethylene) and poly-(vinyl chloride) are suited without a special surface treatment.

Then, the coating layer obtained in this manner is subjected to the monochromatic radiation of the laser, whereby the substrate and the laser beam are movable relative to each other. For instance, the laser beam may be moved in a swinging motion normal to the direction of the forwards moving substrate and will, thereby, initiate the polymerization in the entire area. At a stationary fixed laser beam, the point-shaped concentration of radiation energy, which is typical for a laser and which is directed onto the coated substrate moving below, requires special precautionary features. These features include an installation of optical devices within the path of the laser beam, whereby at least in one direction, preferably in the direction normal to the moving direction of the coated substrate, an expansion of the laser beam will be achieved. Of course, this expansion will also result in a reduction of the energy density in the radiated area. However, due to the high energy of the primary beam, which is one of the particular properties of the laser, there will be a remaining energy density from 0.1 to 320 mJoule / cm^2 , which is sufficient for initiating the polymerization reaction, even at a large expanded, wide-angled beam. It should be mentioned, that the radiation is carried out at room temperature. Of course, the temperature may also deviate from the room temperature, which will, however, not result in any particular advantages. During the polymerization reaction, the layer to be polymerized may show a slight temperature increase. This will, however, not result in any negative side-effects. Since the portion of IR-light, which is usually also present in the light of UV-lamps, will be absent in this case, a cooling will not be needed in most of the cases. However, a particular attention should be given to the oxygen content in the reaction zone, since the oxygen molecules will react with radicals as well known at a rate, which, depending on the monomer, is 10,000 to 1,000,000 -times faster than the actual polymerization reaction. Besides, the oxygen will absorb UV-light at a wavelength of less than 200 nm. The exclusion of oxygen e.g. by selecting an inert atmosphere, such as nitrogen, or by applying a vacuum, may always be indicated, if short reaction times are desired or if the radiation is to be carried out at a wavelength of less than 200 nm. A useful protection may in this case be achieved by covering the substrate to be radiated, with a UV-transparent film.

At a preferred realization of the process according to the invention, the carrier substrate is formed as a film, whereby the possible line-speed defines the length of the self-adherent hydrogel material to be produced per unit time. The line-speed depends on a series of parameters, from which the composition of the mixture, the layer thickness of the mixture and the radiation exposure time have the greatest effect. Since the pulsating lasers will permit effective radiation times of less than 1 second, and at the other hand, the thicker coating layers will require longer radiation times for a polymerization, the exposure times in the process according to the invention are in the range from 10^{-3} to 10^3 seconds, preferably in the range from 10^{-2} to $3 \cdot 10^2$ seconds. The radiation exposure times, which are of interest in a continuously operated production line, are less than 1 second, whereby line-speeds in the meter-range are obtained. Not at last, for obtaining higher line-speeds, it is also possible to use several lasers at the same time, emitting with the same or also different

wavelengths. A geometrically offset double-radiation may also be realized by splitting the primary laser beam into 2 part-beams, which are directed onto the adhesive layer at a defined spacing.

The longer radiation times beyond 1 second are of a particular interest at a discontinuous batchwise execution of the process.

If the layer is coated onto a carrier substrate, which is transparent for a UV-radiation, the radiation may also be carried out from the backside of the substrate, in which case, the laser beam may be guided into the suitable position by means of glass-fiber optics. This kind of radiation may be carried out during or also after the radiation of the upper side. This process variant has particular advantages at the preparation of very thick pressure-sensitive adhesive layers.

At the selection of the process parameters, some fundamental rules have to be observed for obtaining the desired results:

- The shorter the emitted wavelength of the laser, the faster the polymerization rate will be.
- The higher the number of the impulses of the laser, the higher the conversion grade will be.
- The lower the impulse sequence frequency, the higher the molecular weight of the final product will be.

Furthermore, it should be mentioned, that the polymerization inhibitor usually added and present in the monomers, do not have to be removed prior to the polymerization according to the invention.

If the carrier substrate, on which the self-adherent hydrogel is coated, may consist of a continuous endless conveyor belt, whereby after the completion of the polymerization reaction induced by the laser radiation, the formed hydrogel layer will be removed from this conveyor belt and transferred onto another non-sticky substrate and conveyed to the desired further processing station.

In the following, the invention shall be further explained by describing some examples:

In all the described examples, the Excimer-Laser Type LPX 210 (Lambda Physics) was used with the following parameter settings:

Emission wavelength:	351 nm,
Max. Mean Energy Output:	28 W,
Max. Impulse Energy:	320 mJ,
Impulse Duration	30 ns
Max. Impulse Sequence Frequency:	100 Hz

Legend of the employed Abbreviations

AS:	Acrylic acid
MAS:	Methacrylic acid
APS:	β -Acryloyloxy-propionic acid
BA:	Butyl acrylate
2-EHA:	2-Ethylhexyl acrylate
IO:	iso-octyl acrylate
PEG 300:	Poly-(ethylene glycol) with a molecular weight of 300 Dalton
PPG 400:	Poly-(propylene glycol) with a molecular weight of 400 Dalton
GN:	Glycerin
DEA:	Diethanolamine
TEA:	Triethanolamine
ZLI3331:	4-(2-Acryloyloethoxy)-phenyl (2-hydroxy-2-propyl) ketone
ABP:	4-Acryloyloxy benzophenone
PAC:	Phenyl-(1-acryloyloxy) cyclohexyl ketone.

EXAMPLE 1

A starting mixture comprised of:

50 weight-% Acrylic acid,
18 weight-% butyl acrylate,
15 weight-% poly-(ethylene glycol) 300,
15 weight-% diethanolamine and
2 weight-% 4-(2-acryloyloethoxy)-phenyl (2-hydroxy-2-propyl) ketone,

is placed at room temperature into a tray of poly-(tetrafluoroethylene) (PTFE) with a plane bottom, whereby the obtained layer thickness amounted to 1000 μm . Then, this mixture was subjected to a laser beam radiation operated under the following conditions:

Applied absolute energy:	160 mJ
Applied Impulse Sequence Frequency:	5 Hz
Energy density:	35.6 mJ /cm ²
Number of Impulses:	400
Radiation time:	80 s.

The obtained self-adherent hydrogel was removed from the tray and was used in the subsequent tests for determining the water absorption.

EXAMPLES 2 TO 15

In analogy to the procedure described in example 1, self-adherent hydrogels were prepared by using compositions as summarized in table 1.

Determination of the Water Absorption

From the hydrogels prepared by means of a laser radiation, a squared sample (2.5 cm x 2.5 cm) was cut out and placed into distilled water at room temperature for 6 hours. The water absorption was determined by determining the weight difference between the water-containing hydrogel samples and the hydrogel samples in the dry state. The determined values of the water absorption are summarized in table 2 and are graphically illustrated in fig. 1 for selected self-adherent hydrogels.

Table 1

Compositions of the self-adherent Hydrogels prepared by means of a Laser Beam Radiation

example	Vinyl carboxylic acid [weight-%]			(Meth)acrylic alkyl ester [weight-%]			Polyoxyalkylene/ Glycerin [weight-%]				Hydroxyl groups containing Amine [weight-%]			Photo-Initiator [weight-%]		
	AS	MAS	APS	BA	2-EHA	IO	PEG 300	PPG 400	GN	DEA	TEA	TIEA	ZLI 3331	ABP	PAC	
2	10	--	--	--	10	--	19	--	--	--	10	--	1	--	--	--
3	40	--	--	14	--	--	--	--	30	--	15	--	--	1	--	--
4	--	--	30	15	--	15	10	--	8	20	--	--	--	--	2	--
5	30	10	--	--	30	--	--	13	--	--	--	14	2	1	--	--
6	--	10	15	--	15	--	20	--	20	--	15	--	5	--	--	--
7	40	--	--	--	--	20	--	26	--	12	--	--	1	--	1	--
8	30	--	--	10	--	--	--	--	40	10	--	8	--	2	--	--
9	--	10	40	--	--	15	15	--	--	--	17	--	1.5	--	--	1.5
10	20	--	10	17	--	--	18	--	20	12	--	--	3	--	--	--
11	35	--	--	--	15	--	20	--	12	--	10	5	--	3	--	--
12	--	10	30	29	--	--	--	--	15	--	15	--	1	--	--	--
13	--	--	40	--	--	16	--	30	--	11	--	--	2	1	--	--
14	40	--	--	--	30	--	14	--	--	--	13	--	--	--	3	--
15	25	--	25	5	10	--	10	--	5	18	--	--	1.5	0.5	--	--

Table 2

Water Absorption of self-adherent Hydrogels prepared by means of a Laser Beam Radiation

Example	Water Absorption [weight-%] after					
	1h	2h	3h	4h	5h	6h
1	986	2303	3458	4477	4971	5819
2	673	1405	2233	3293	4268	5120
3	813	1916	2830	3866	4512	5482
4	780	1830	2010	3335	4290	5188
5	762	1750	1980	3066	4012	4962
6	750	1700	1830	2860	3844	4725
7	948	2216	3337	4268	4863	5728
8	886	2116	3216	4198	4711	5614
9	880	2194	3311	4216	4768	5681
10	916	2086	3216	4322	4819	5632
11	942	2223	3412	4422	4912	5689
12	813	1986	3028	4001	4316	5217
13	771	1812	2788	3844	4211	5083
14	863	2002	2993	3930	4719	5556
15	808	1910	2717	3784	4526	5461

PATENT CLAIMS

1. A process for preparing self-adherent hydrogels by a radicalic polymerization of a photo-polymerizable, solvent-free starting mixture by means of a UV-radiation in the range from 180 to 400 nm, whereby the energy needed for initiating the polymerization reaction, is introduced by means of a monochromatic radiation of a laser, wherein the polymerizable, solvent-free starting mixture contains the following components:
 - A- a vinyl carboxylic acid,
 - B- an alkyl (meth)acrylate with 1 to 12 carbon atoms in the alkyl group,
 - C- a polyoxyalkylene with a molecular weight of up to 2000 Dalton, and glycerin or its esters,
 - D- a hydroxyl groups containing amine,
 - E- a photo-initiator.
2. A process according to claim 1, wherein the components of the starting mixture are preferably employed in the following concentration:
 - A- a vinyl carboxylic acid, 30 to 60 weight-%,
 - B- an alkyl (meth)acrylate with 1 to 12 carbon atoms in the alkyl group, 10 to 30 weight-%,
 - C- a polyoxyalkylene with a molecular weight of up to 2000 Dalton, and glycerin or its esters, 10 to 40 weight-%,
 - D- a hydroxyl groups containing amine, 10 to 20 weight-%,
 - E- a photo-initiator, 1 to 5 weight-%.
3. A process according to claim 1 or 2, wherein the vinyl carboxylic acid is selected from the group comprised of acrylic acid, β -acryloyloxypropionic acid, vinylacetic acid, itaconic acid, methacrylic acid, aconitic acid fumaric acid, trichloroacrylic acid and dimethylacrylic acid.
4. A process according to claim 1 or 2, wherein the alkyl (meth)acrylate with 1 to 12 carbon atoms in the alkyl group is selected from the group comprised of methyl-, ethyl-, propyl-, isopropyl-, butyl-, isobutyl-, hexyl-, heptyl-, 2-ethylhexyl-, 2-methylheptyl-, iso-octyl-, nonyl-, isononyl-, decyl-, isodecyl- or dodecyl (meth)acrylate.
5. A process according to claim 1 or 2, wherein the polyoxyalkylene with a molecular weight of up to 2000 Dalton is comprised of a poly-(oxyethylene), poly-(oxypropylene) or a copolymer of ethylene oxide and propylene oxide.
6. A process according to one or several of the claims 1 to 5, wherein the hydroxyl groups containing amine is an ethoxylated amine or is selected from the group comprised of diethanolamine, triethanolamine, N-methyl-diethanolamine, tri-isoethanolamine, 2-amino-2-methyl-1,3-propanediol, tris-(hydroxymethyl-) aminomethane or dimethyl-ethanolamine.
7. A process according to claim 1 or 2, wherein the photo-initiator is selected from the group comprised of acetophenone, benzophenone, benzil derivatives, benzoin derivatives,

dialkoxyacetophenone, hydroxyalkylphenone, α -acyloxime esters, α -halogenketones, thioxanthenes, fluorenone derivatives or Michler's ketone.

8. A process according to claim 1, wherein a pulsating laser is employed.
9. A process according to claim (?), wherein the laser beam generates an energy density from 0.1 to 320 mJoule /cm².
10. A process according to one or several of the preceding claims, wherein the starting mixture areally distributed in a layer thickness from 50 to 5000 μ m, is subjected to the monochromatic laser beam radiation.
11. A process according to one or several of the preceding claims, wherein the exposure time to the UV-laser radiation is in the range from 10⁻⁹ to 10³ seconds.
12. A process according to claim 11, wherein the exposure time is in the range from 10⁻² to 3 · 10² seconds.
13. A process according to one or several of the preceding claims, wherein the UV-radiation is carried out under the exclusion of oxygen.
14. A process according to one or several of the preceding claims, wherein the polymerization is carried out in a continuous manner under a relative movement of the laser beam and the starting mixture to each other.
15. A process according to one or several of the preceding claims, wherein the starting mixture is radiated by a laser beam, which is expanded (diverged) in at least one direction by means of an optical device.
16. A process according to one or several of the preceding claims, wherein several lasers are simultaneously or consecutively employed for carrying out the polymerization reaction, whereby these lasers may have the same or a different emission wavelength.
17. The usage of the self-adherent hydrogels according to claims 1 to 16 in non-sterile or sterile forms as wound covers.

1 Page with drawings is attached.

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Fig. 1

